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Georgia kaolin as the China Clay constituent in floor and wall tile bodies

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GEORGIA KAOLIN AS THE CHINA CLAY CONSTITUENT
IN
FLOOR AND WALL TILE BODIES

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GEORGIA KAOLIN AS THE CHINA CLAY CONSTITUENT IN FLOOR AND WALL TILE BODIES

INTRODUCTION

The replacement of the China Clay content in vitreous floor tile and porous wall tile bodies wholly by Georgia sedimentary kaolin would reduce the cost of these bodies being used in our floor and wall tile plants at present. This plastic kaolin is available in large quantities in the State of Georgia, covering an area of about 7500 square miles, (1). It is the intention of this work to substitute this American Clay for the more costly imported English China Clay now being used.

A.V. Beininger (2) found that Georgia kaolin is a sticky, fine grained, refractory or ball clay which is very resistant to heat and does not melt until temperatures of from 1750 to 1800 degrees Centigrade are reached. He also brought forth the following determination:

Chemical Analysis of Georgia Kaolin

SiO_2 ------	46.86%
Al_2O_3 ------	38.67%
Fe_2O_3 ------	00.57%
CaO ------	00.55%
MgO ------	00.25%
K_2O ------	00.27%
Na_2O ------	00.49%
H_2O ------	13.27%

H. Ries (3), who has worked with a great number of these Georgia kaolins, says the high bisque loss and excessive shrinkage is probably a serious problem in using these fine sedimentary clays, but this difficulty can be overcome by proper body mixes and blending of the clay.

According to G.H. Brown (4), Georgia kaolin shows a heat of absorption beginning at 525 degrees Fahrenheit, which is most pronounced between 530 and 590 degrees Fahrenheit. Loss in weight of clay equals 12.93% at 650 degrees Fahrenheit. A large loss in plasticity is brought about by heating at 750 degrees Fahrenheit, and at 800 degrees Fahrenheit the plasticity is destroyed. This clay also shows a volume shrinkage somewhat similar to that of North Carolina kaolin, which is greater, however, at higher temperatures.

Keeping the above considerations in mind, the object of the investigation as carried out was to produce a cheaper tile body, which would embody in its composition Georgia kaolin in place of English China Clay.

MATERIALS

The raw materials used to make up the bodies in the study consisted primarily of washed Georgia kaolin, Pennsylvania flint, Buckingham feldspar, No. 5 Tennessee ball clay, heavy MgO, $MgCO_3$ (C.P.), $CaCO_3$ (C.P.), and $BaCO_3$ (C.P.). Distilled water was used as a tempering medium for all the bodies.

PROCEDURE

In order to have some basis upon which to begin the investigation, three bodies containing as high as 35% English China Clay as a clay constituent were selected for the end members of a 21-member triaxial system. The China Clay content in each body was replaced with washed Georgia kaolin from the Macon District.

Table I

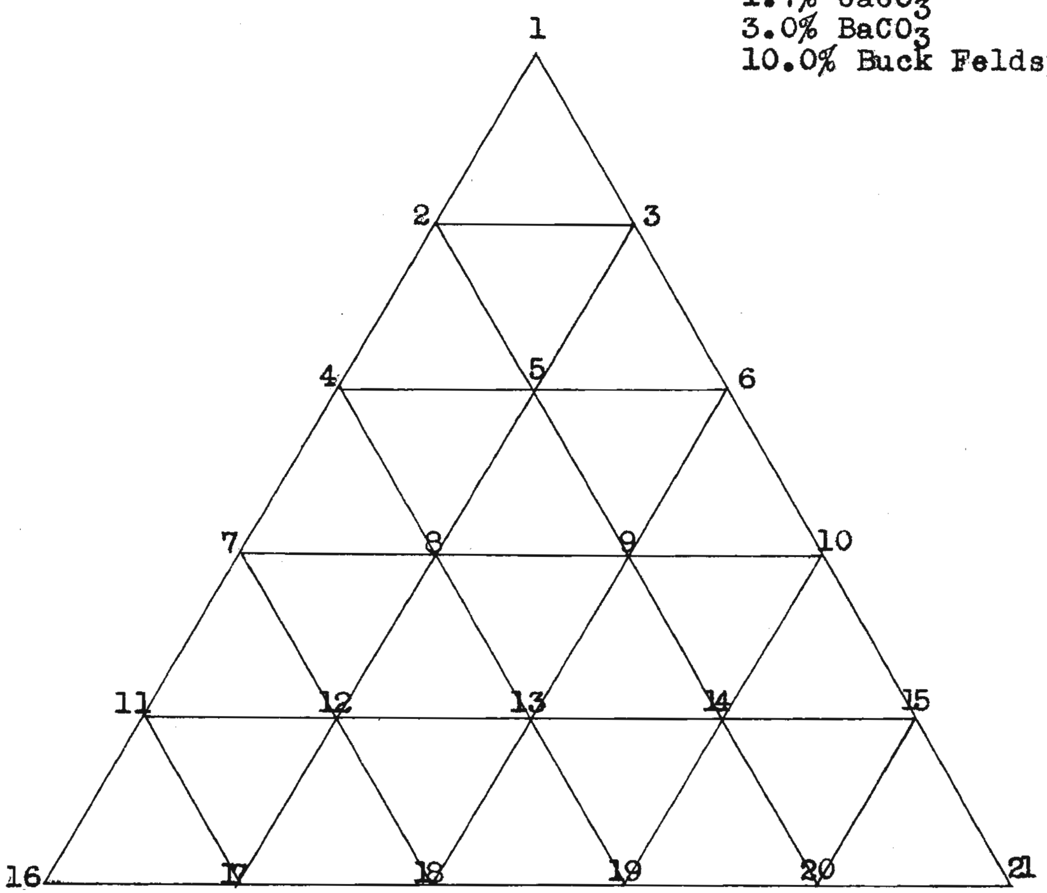
	No.1	No.16	No. 21
Flint-------------	50.0%	19.8%	35.0%
Georgia Kaolin---	35.0%	29.7%	35.0%
$MgCO_3$----------	0.3%		
$CaCO_3$----------	1.7%		
$BaCO_3$----------	3.0%		
MgO (heavy)----		1.0%	
Buck.Spar.--------	10.0%	39.6%	20.0%
Tenn.B. Clay #5--		9.9%	10.0%

Body 1 was obtained from C.M. Dodd (5) and contains 15% of a flux as shown in the above table.

Bodies 16 and 21 as given by G.A. Bole (6) and Radcliffe (7) were used as the other end members of the triaxial system.

FIGURE I

50% Flint
35% Georgia kaolin
0.3% MgO
1.7% $CaCO_3$
3.0% $BaCO_3$
10.0% Buck Feldspar



19.8% Flint
29.7% Georgia kaolin
1.0% Heavy MgO
9.9% Tenn. Ball Clay
39.6% Buck Feldspar

35% Flint
35% Georgia kaolin
10% Tenn. Ball Clay
20% Buck Feldspar

TABLE II

Member	Flint	Georgia Kaolin	$MgCO_3$	MgO	$CaCo_3$	$BaCO_3$	Buck Feldspar	Tenn. B. Clay No. 5
1	50.0%	35.0%	0.3%		1.7%	3.0%	10.0%	
2	43.9	34.0	0.3	0.2	1.4	2.3	15.9	2.0
3	47.0	35.0	0.3		1.4	2.3	12.0	2.0
4	37.9	32.9	0.2	0.4	1.0	1.8	21.8	4.0
5	41.0	34.0	0.2	0.2	1.0	1.7	17.9	4.0
6	43.9	35.0	0.2		0.9	1.8	14.0	4.0
7	31.9	31.9	0.1	0.6	0.7	1.2	27.8	6.0
8	35.0	32.8	0.1	0.4	0.7	1.1	23.8	6.0
9	37.9	34.0	0.1	0.2	0.7	1.1	20.0	6.0
10	41.0	35.0	0.1		0.7	1.2	16.0	6.0
11	25.8	30.7	0.1	0.8	0.4	0.6	33.6	8.0
12	29.0	31.8	0.1	0.5	0.3	0.6	29.8	7.9
13	31.9	32.9	0.1	0.4	0.4	0.6	25.8	7.9
14	37.2	29.7	0.1	0.2	0.4	0.6	23.4	8.4
15	38.0	35.0	0.1		0.3	0.6	18.0	8.0
16	19.8	29.7		1.0			39.6	9.9
17	22.8	30.8	0.8				35.7	9.9
18	25.9	31.8	0.6				31.8	9.9
19	28.9	32.9	0.4				27.9	9.9
20	32.0	33.9	0.2				24.0	9.9
21	35.0	35.0					20.0	10.0

Table 2, shows the percentage composition of the members of the 21-member triaxial system.

Preparation of Bodies

1. A 1500 gram batch of each member was ground for three hours in a porcelain lined, pebble mill, the water and raw materials being mixed before adding to the mill.

2. The slip was then screened through a 60 mesh screen and dewatered on plaster blocks.

3. The bodies as removed from the plaster were dried and pulverized to pass 40 mesh, after which the necessary water was added to bring the moisture content of each member up to 11% of its weight (dry basis). By sprinkling, the water on the bodies, kneading with the hands, and rescreening through a 20 mesh screen, the additional moisture was added successfully. The prepared bodies were placed in air tight glass jars and aged 24 hours so as to thoroughly distribute the moisture.

Method of Making Tile

Each body was molded into 3" by 1½" tile and 8" by 1" by 1" bars for testing. Five test bars and three tile were made to determine the properties of the body. The dust was pressed in a hand screw dry press at a pressure which materially depended on the human element. No loss in trimming or handling was experienced. The tile and bars were dried in an electric drier at 150°C., placed in saggers and burned to cone 9 in a down draft, direct oil fired kiln (cone9 indicates the heat treatment received inside the saggers). A 26 hour firing schedule was followed, the temperature rise being 60° Centigrade per hour with a four hour soaking period at the end of the burn.

Standard methods were used in securing the data contained in Table III and table IV.

TABLE III

Body No.	% Moisture	% Fired Shrink	Fired M of R	% Absorpt.
1.	8.47	7.70	4040	4.12
2.	8.95	9.32	5720	2.69
3.	8.28	8.60	4850	4.90
4.	9.25	10.71	5700	0.47
5.	7.54	10.10	3920	2.94
6.	10.81	7.40	4530	7.10
7.	9.44	11.50	5100	0.46
8.	9.87	10.30	4750	0.45
9.	7.35	9.80	4440	1.28
10.	9.58	8.90	4150	4.50
11.	11.28	12.40	3980	0.48
12.	9.62	11.70	6000	0.29
13.	9.42	10.37	3980	0.70
14.	7.45	9.40	4075	0.69
15.	8.00	8.50	3620	3.74
16.	9.77	11.90	6300	0.15
17.	10.61	10.90	3120	0.32
18.	9.80	9.70	2480	0.60
19.	8.97	9.20	2790	1.54
20.	10.40	8.00	2500	2.70
21.	9.93	6.50	1900	6.60

From the data on the members of the triaxial, it was then possible to select bodies for consideration in making floor and wall tiles. The tiles in general had a slight ivory tinge probably due to impurities in the Georgia kaolin which were not removed in the washing process.

FLOOR TILE

Bodies 4,7,12 and 16 were selected as good floor tile bodies because of their low absorption (all under 1%) and their good strength (above 5000 lbs. per sq. in. modulus of rupture). Since all of the bodies had a tinge of ivory in varying degrees, new ones were made for the members selected with a series of cobalt stain additions to act as neutralizers. According to Bleininger (2), cobalt stain when added properly will tend to have a neutralizing effect of turning the yellow to a less noticeable green.

The proper way to add the cobalt stain is in the form of cobalt carbonate which is easily mixed evenly through the body. To prepare cobalt carbonate, dissolve 15 grams of pure cobalt sulphate in 750 grams distilled water. Then add 7.5 grams of sodium carbonate and stir thoroughly, the cobalt carbonate gradually precipitating out. One gram of this stain will satisfactorly neutralize 20 lbs. of dry body.

The procedure followed for making these bodies in the triaxial system was duplicated using 1500 gram mixes with the exception that the amounts of cobalt stain as shown in Table IV were added to the body in the ball mill just before grinding. Only the 3" by $1\frac{1}{2}$" tile were pressed in this study.

Table IV

	No. 4	No. 7	No. 12	No. 16
Cobalt Carbonate Ratios --	0.5cc	1.0cc	1.5cc	2.0cc
Color --	Ivory	Light Ivory	White	Greenish White

Two sets of tile for each body were made, one set being fired to cone 9 in 26 hours and the other to cone 8 in 20 hours (inside saggers).

WALL TILE

Bodies 1,3,6, and 21 were selected for desirable wall tile bodies because of their higher absorption (all above 4%) which makes it possible for a glaze to stick to them. Their color was better too, although an addition of cobalt stain (1.5cc ratio) was necessary to give a good white body.

As in the case of members selected for prospective floor tile bodies, new batches of these four members were made up following the same procedure as used in all other runs. Each body was made up into 3" by 1½" tile only. A part of the tile was calcined (at 1000° C.) in an electric muffle before being sprayed as described in Burn No. 1 and Burn No. 2.

<u>Burn No. 1:</u> An equal number of dried and colored tile

from the four prospective wall tile bodies were sprayed with a cone 9 porcelain glaze of the following composition:

.25 Na_2O		
.65 CaO	.35 Al_2O_3	3.0 SiO_2
.05 BaO		0.1 B_2O_3
.05 MgO	Applied at 1.45 Sp.Gr.	

The slip was applied with an air gun two coats being sprayed on each tile.

Burn No. 2: The remaining dried and colored tile were sprayed with a cone 8 raw lead glaze especially adaptable to wall tile.

Glaze composition (7):

.2 K_2O		
.3 CaO	.30 Al_2O_3	1.5 SiO_2
.5 PbO	Applied at 1.42 Sp.Gr.	

DISCUSSION OF RESULTS

All the bodies resulting from the triaxial study showed relatively low absorption, one having only 0.15%. There was no lose due to cracking or warping during the drying or burning operations.

Bodies towards the (No. 16) corner of the triaxial study showed greater vitrification than did the bodies toward the other two end members.

And member No. 1 and the surrounding members showed a better color than the rest, a number comparing favorably with commercial production.

FLOOR TILE

From observations made on the floor tile bodies, it was shown that the tile gave better results when fired to cone 8 than to cone 9, as was the case in the first run.

The addition of small amounts of cobalt stain gave evidence of neutralizing the ivory color. With 1.5 cc of stain, the color apparently was neutralized to a good white.

WALL TILE

There were no specks visible in any of the specimens, indicating the Georgia kaolin used was well washed.

The tile showed a slight tendency to warp when fired to cone 9 but was perfect when taken only to cone 8. This indicates that at cone 9 these tile begin to overfire.

The color of the glazed ware appeared whiter with the cone 8 raw lead glaze than with the cone 9 porcelain glaze. Also the former did not fit the bodies as well as did the cone 8 glaze.

CONCLUSIONS

Since only one kind of Georgia kaolin was available for this work, the results are limited in scope because of the lack of uniformity in the different deposits. Some of them burn to a good white while many others burn to a cream color due to colloidual iron oxide present which cannot be removed by washing.

From this work in which the Georgia kaolin was substituted for the china clay constituent in floor and wall tile bodies, it is concluded that;

(1). In preparation of the bodies, the Georgia kaolin works fully as well as English China clay.

(2). The loss in trimming and handling tile is no more than in the tile bodies used at present.

(3). As far as cracking and warping during the drying and burning operations are concerned, these bodies came out in a perfect condition when fired to Cone 8.

(4). Slight discoloration in a number of the bodies was successfully neutralized by a very small addition of cobalt carbonate.

(5). In the case of the glazed wall tile, the bodies had such absorption values as to easily take a porcelain or raw lead glaze. By calcining the tile to 1000° C before spraying them, even better results were obtained.

(6). It is concluded here that in dry pressed bodies of small size such as floor and wall tile, Georgia kaolin would work better than in larger shapes where shrinkage is a factor.

RECOMMENDATIONS

For further work on this subject it would be advisable to go into the kaolin-flint ratio in an attempt to reduce shrinkage and to improve whiteness. (5) To make such a study, it would be necessary to select a body, such as (No.2) and while keeping the other ingredience constant, vary the kaolin and flint content to get maximum whiteness and reduce shrinkage. A study of this nature would aid in making possible the use of Georgia kaolin in floor tile and wall tile bodies.

An intensive study could be made on the proper body mixes and blending of Georgia kaolins in wall tile bodies using these fine-grained sedimentary kaolins which would in turn cut down the high bisque loss and excessive shrinkage.

A further study on the correct amounts of cobalt stain to be used and the form in which it should be introduced in connecting the slight variation from white shown by these various Georgia clays offers an interesting problem for investigation.

Determining the effect of a reducing atmosphere on the iron content in the Georgia kaolins in an attempt to get away from the ivory tinge in the whiteware bodies could be made worth while.

Developing suitable raw lead glazes for this type of wall tile body might prove to be another interesting line of investigation.

APPLICATION TO THE INDUSTRY

Since the shipment of Georgia Kaolin used in this investigation was thoroughly washed before being used, this eliminated the possibility of impurities in the clay other than colloidual iron oxide which cannot be removed by washing. But, due to lack of uniformity, many different types of kaolin might be encountered in the industry.

These kaolins when washed yield a high precentage of washed product, and certain deposits contain beds of bauxite or bauxite clay associated with the white clay (8).

Up to the present time this washing process has been so expensive that it did not pay the operators of the pits to remain in business. Thus, we see that to make it possible for these clays to be used in the industry in place of English China Clay as the clay ingredient in floor and wall tile bodies, the cost of removing the impurities must be reduced to a minimum. However, this is another problem for further investigation before Georgia kaolins can be used successfully in the industry.

Other than the objection to the cost of washing there seems to be no doubt that the foregoing work has shown Georgia kaolin to be a possible substitute for English China Clay in the manufacture of floor and wall tile.

Even with the high washing cost of Georgia kaolin it can be produced more cheaply than English China Clay can be imported.

Therefore any reduction in washing costs which might be effected by larger production due to extended usage, would further lower the cost of tile made from this kaolin.

ACKNOWLEDGMENT

I wish to acknowledge the kind assistance and practical advice rendered by Professor C.M. Dodd, of the Ceramic Department.

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J.A.C.S. Vol. 6 (1923) P. 854

(7). Radcliffe - Tile Bodies
T.A.C.S. Vol. 16 P. 127

(8). H.F. Staley - Raw Lead Glazes For Wall Tile
T.A.C.S. Vol. 15 P. 695

ABSTRACTS

Use of Sedimentary Kaolins of Georgia in Whitewares

G.A. Bole and R.T. Stull   T.A.C.S. Vol. 6 P. 854 (1923)

Sproat's work on the mining and working method used in the Dry Branch District of Georgia proved an interest to the ceramic industry.

The working properties and fired tests were made on five samples of kaolin from different localities in Georgia. Following are the results obtained:

Table I

Working Properties and Firing Tests

Clay	% H_2O of P.	% Vol. Shrink	Drying Behavior	% Vol. Shrink
1	31.76	11.56	poor	13.83
2	33.60	15.40	Fair	11.76
3	35.20	19.71	good	18.10
4	38.73	15.83	Fair	14.63
5	43.30	20.90	Fair	12.69

See next page for Table II

Table II

Clay	Cone 01 % Porosity	Burning Behavior	Color No.	Vol. Shrink	Cone 11 % Porosity	Color No.	Cone
1	50.71	poor	white	25.40	41.25	tan	34
2	42.81	Fair	White	35.04	24.41	tan	34
3	40.81	Fair	tan	41.88	13.62	brown	35
4	44.20	good	white	37.32	25.72	tan	34.5
5	46.20	good	white	36.43	26.96	brown	34

Bleininger states that the slight variation from white shown by these clays can be corrected by the use of cobalt stain.

Classification of Floor Tile as Related to Degree of Vitrification

T.A.C.S. Vol. 17 P. 484

When feldspar, ball clays, and china clays were utilized in the blending of floor-tile bodies which were fried at high temperatures, the vitreous or practically impervious tile became a reality. Into these blends have been introduced the coloring oxides adapted to high temperatures as cobalt oxide, chrominum oxides, etc. for a line of colors (vitreous) constituting the white and colored vitreous tile of today.

There yet remains, however, a field for those tile whose color is produced by the development in the fire of the natural color of the clay composition. Attempts to obtain the vitreous by firing these clays to higher temperatures results in over firing and inferior tile.

NOTICE: The class to which floor-tile shall be determined is by the amount of water they will absorb. Absorption shall be determined by immersing the tile in boiling water for one hour followed by soaking in the same water for 24 hours. Average results shall be obtained from not less than five tile and be expressed in terms of percent of dry weight. Classification as to the amount of absorption will be as follows:

0 - 2%	absorption	=	Vitreous
2 - 10%	"	=	Semi-vitreous
10 - ?%	"	=	Plain unglazed

Moisture Content on Dry Press Floor Tile

T.A.C.S. Vol. 19 P. 409 (1917)

The moisture content is as follows:

Low	amount	of	water	=	7.9%
High	"	"	"	=	14.2%
Average	"	"	"	=	11.3%

Method of Pressing:

1. Plunger of press is allowed to enter box slowly to eliminate a large portion of the air.

2. The plunger is then raised to a constant point and allowed to drop on the piece under the influence of its own weight and momentum.

3.. Any number of applications maybe made.

Kaolin ReFining (I.E. Sproat)

T.A.C.S. Vol. 18 P. 767

The author gives us both the ordinary washing operation in which blunging machines and settling troughs are used and also the ($NaOH$ - H_2SO_4) process of refining kaolin, which is thoroughly practical. This theory utilizes the principles of colloidual chemistry.

Dehydration of Georgia Kaolin (Brown)

T.A.C.S. Vol. 14 P. 709

This article gives the heat of absorption, loss in weight when heated at constant temperatures, loss in plasticity due to heating to constant weight at different temperatures, and the volume shrinkage for a sample of Georgia kaolin.

Effect of Some Electrolytes on Georgia Kaolin

T.A.C.S. Vol. 10 P. 520

Both $CaCl_2$ and $AlCl_3$ are more effective than NaCl on the volume shrinkage of Georgia kaolin in proportions less than 0.04%. 0.05% NaCl gives same decrease in volume shrinkage as smaller proportions of the other chlorides.

Clays For Tiles

Tonind Ztg. 44, 1177(1920) P. 117

The main requirements are absence of useless impurities, clearness of the fired color, and vitrescibility. The vitrification point should not be near a softening point. A satisfactory clay is one which is free from lime, gypsum and pyrite, and is moderately refractory. Thoroughly vitrified ware requires a uniform body.

Distribution of Kaolin and Bauxite of the Coastal Plain of Georgia (R.T. Stull)

J.A.C.S. Vol. 7 P. 513 (1924)

Commercial deposits of sedimentary kaolins and bauxites occur in the lower Cretaceous of the coastal plain. These kaolins vary from "hard clay" on one hand to "soft clay" on the other. Hardness of the clays apparently depends on the free silic acid content, and they are difficult to slake and filter press. The soft clays are washed for the filler and ceramic trades.

The Use of Georgia Kaolins in a Semi-porcelain Body

(Hemsteger and Stief)

J.A.C.S. Vol. 9 (1926)

Georgia kaolin added to this type of body enables a higher flint content to be used, also imparting greater dry strength to the body.

General Consideration of Floor Tile Bodies Made From Clays (R.C. Purdy)

T.A.C.S. Vol. 7 P.95

Purdy divides floor tile made from clay into two classes:

(a). Those composed of a prepared facing body on a common clay back-ground.

(b). Tile of different shapes with solid bodies. He discusses both classes in detail.
